Organic Aqueous Flow Batteries for Massive Electrical Energy Storage

Roy G. Gordon[1,2], Alán Aspuru-Guzik[2] & Michael J. Aziz[1]

[1] Harvard School of Engineering & Applied Sciences
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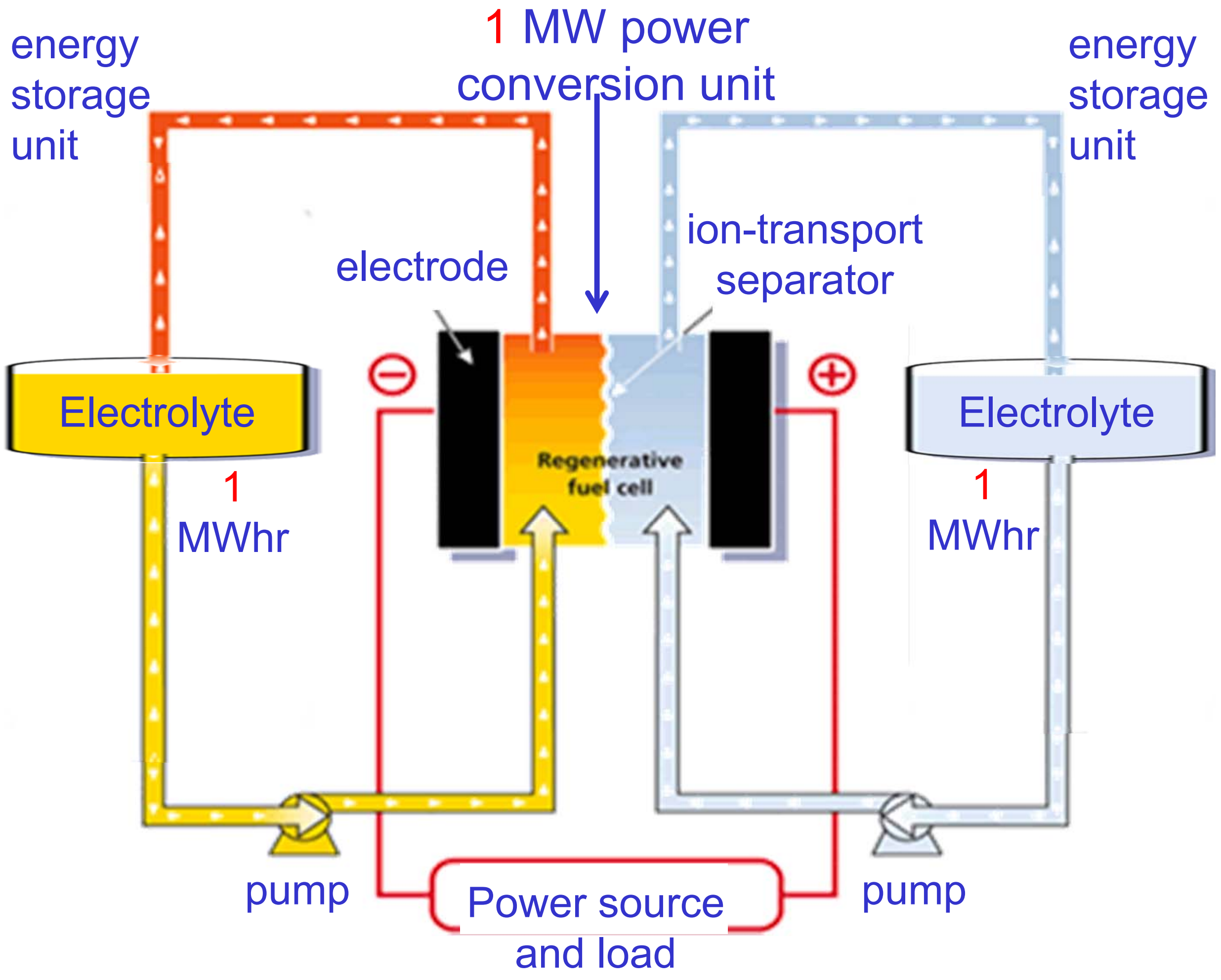
- **Quinone electrochemistry**
- **Acid quinone RFB**
- **Alkaline quinone RFB**
- **Aza-aromatic alkaline RFB**
- **Neutral pH RFB**
- **Prospects for ultra-low cost storage**

International Battery Seminar, Ft. Lauderdale, 3/23/2017

Flow Batteries Independently Size Energy and Power

Requirements for Efficient Storage, 1 MW nameplate		
	Solar	**Wind**
Power	1 MW	1 MW
Energy	16 MWhr	60 MWhr
$\frac{\text{energy}}{\text{power}}$ Ratio	16 hr	60 hr



based on image from vrbpower.com

J. Rugolo and M.J. Aziz, "Electricity Storage for Intermittent Renewable Sources", *Energy Environ. Sci.* **5**, 7151 (2012)

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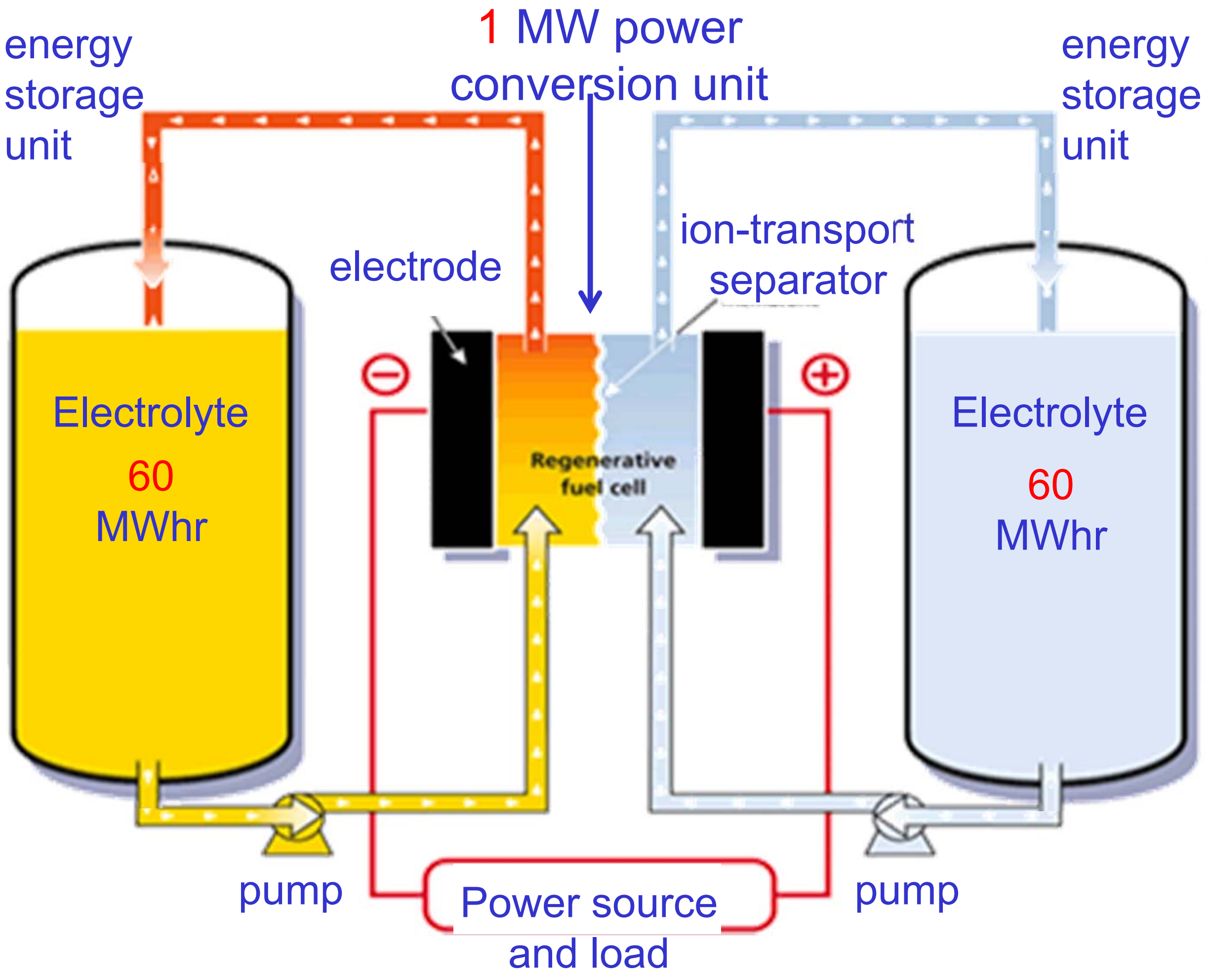
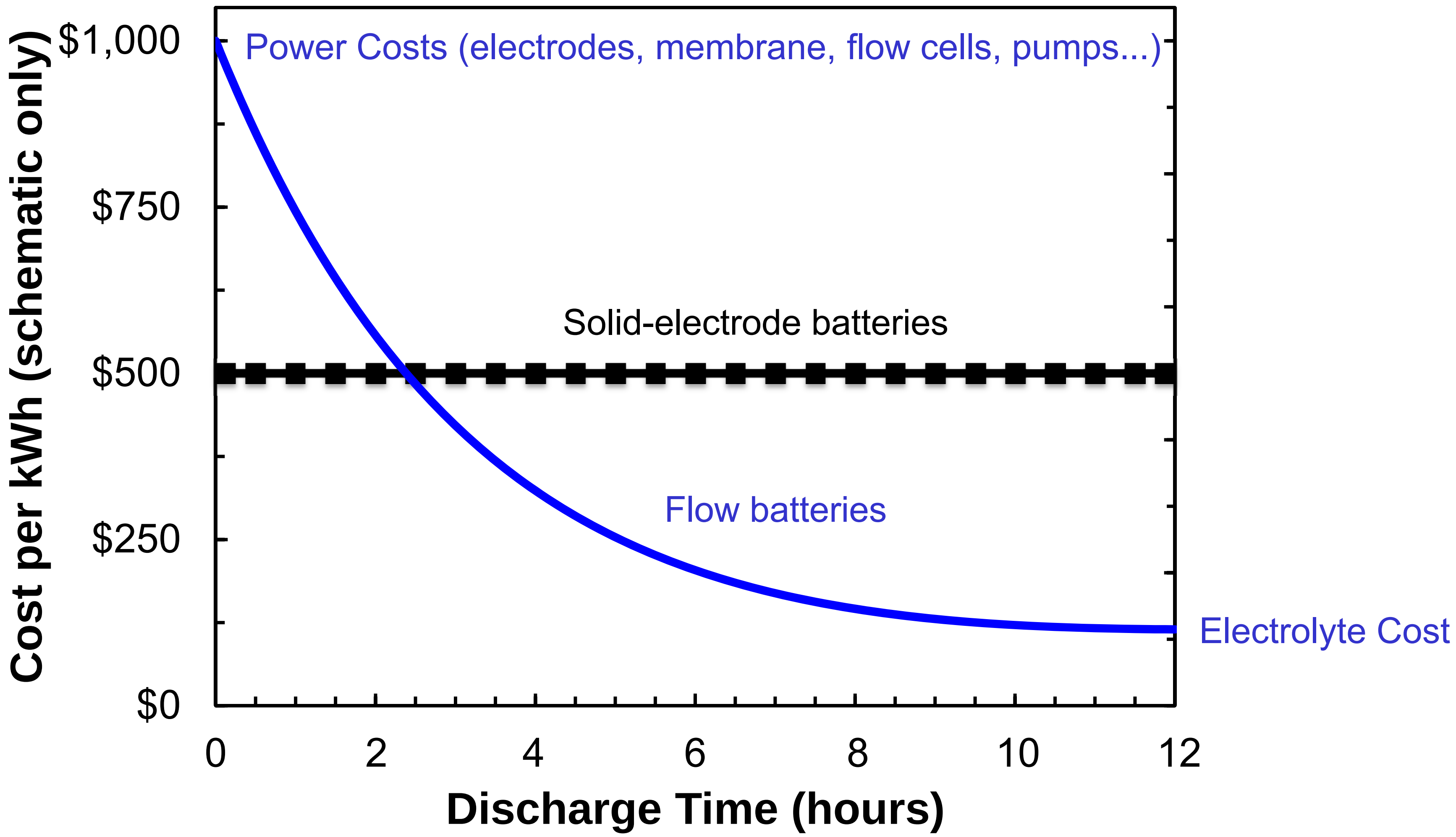


based on image from vrbpower.com

J. Rugolo and M.J. Aziz, "Electricity Storage for Intermittent Renewable Sources", *Energy Environ. Sci.* **5**, 7151 (2012)

Flow Batteries Decrease Cost for Long Duration Discharge



Vanadium Redox Flow Battery: the Most Commercialized RFB

Vanadium 1 MW x 5 hr flow battery installed at a PV farm (Sumitomo Electric)

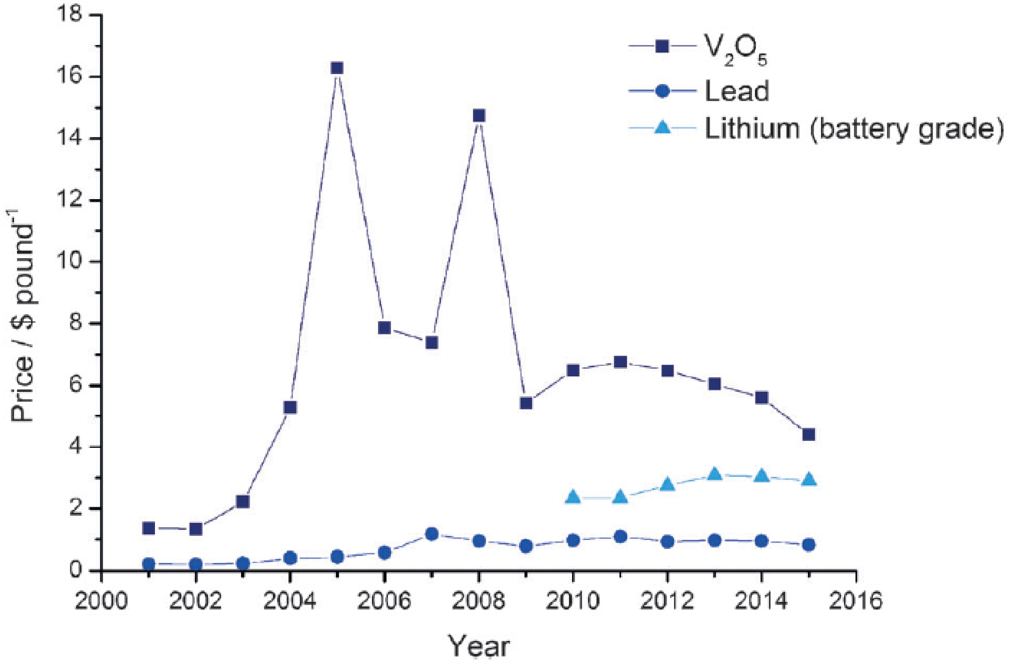
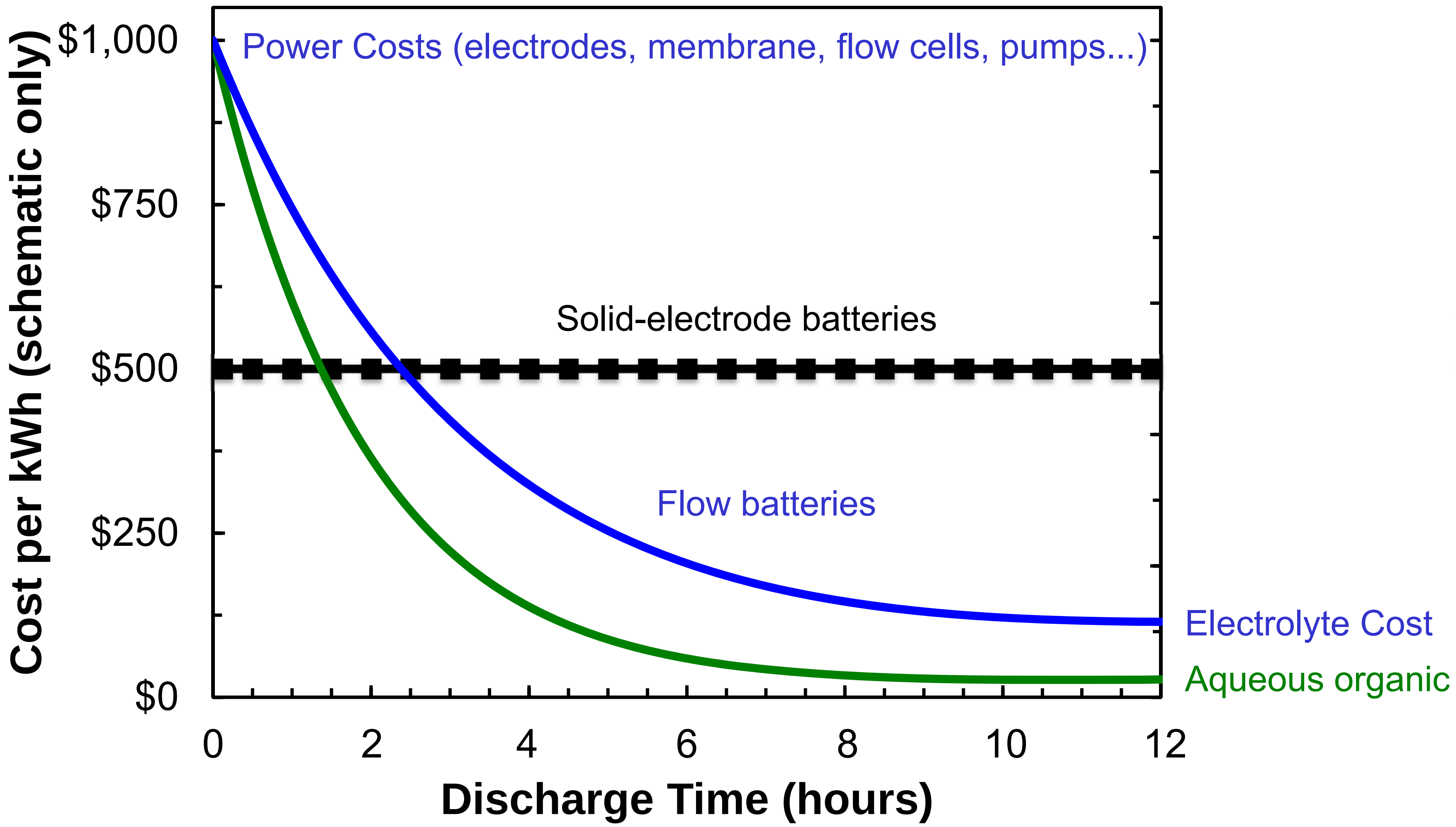


Figure 3. Commodity prices of Li (battery grade), Pb, and V_2O_5 (standard grade). Data obtained from the U.S. geological survey.

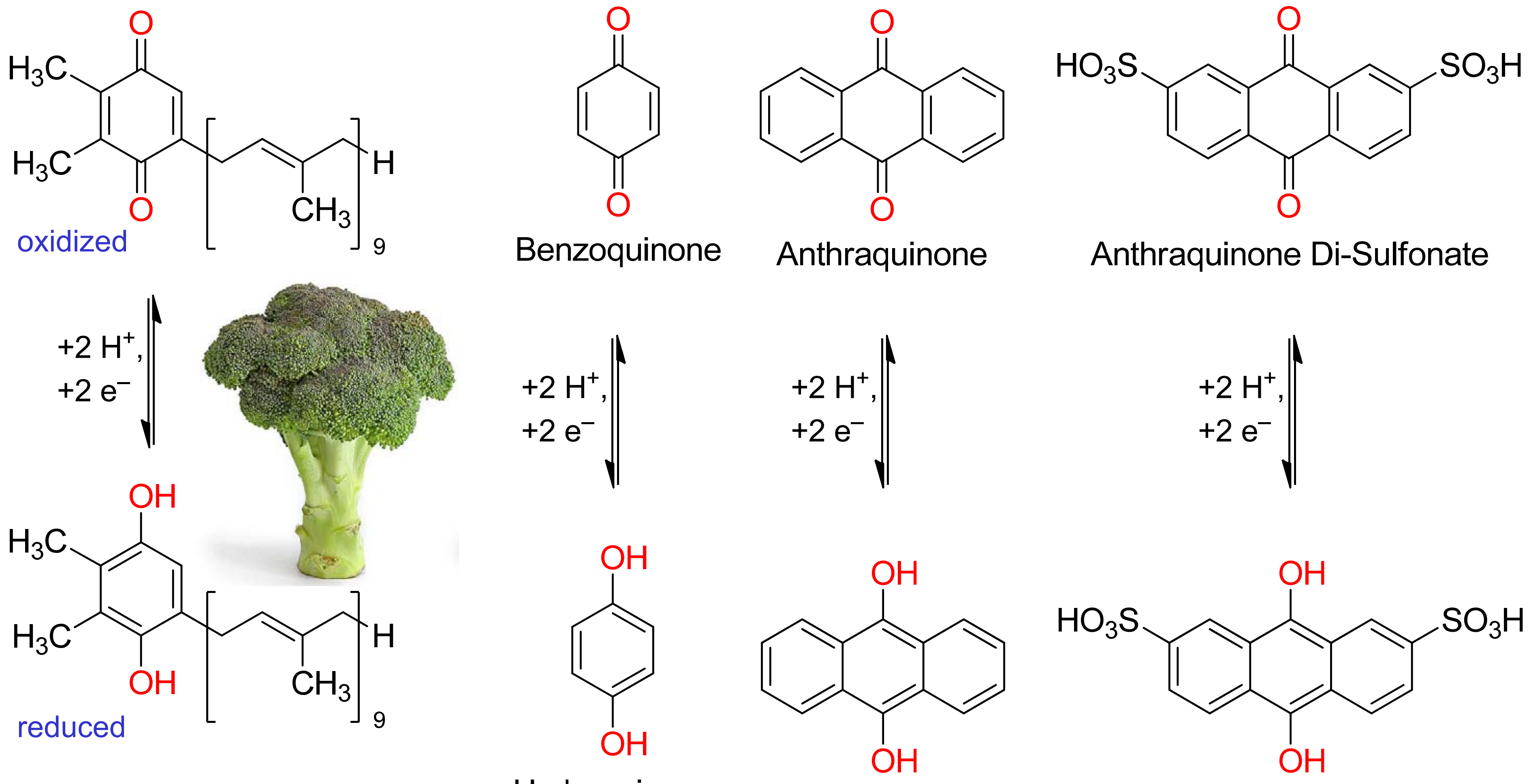
J. Winsberg *et al.*, "Redox-Flow Batteries: From Metals to Organic Redox-Active Materials", *Angew. Chem.* (2016)

Cost of Chemicals Sets Floor on System Cost / kWh



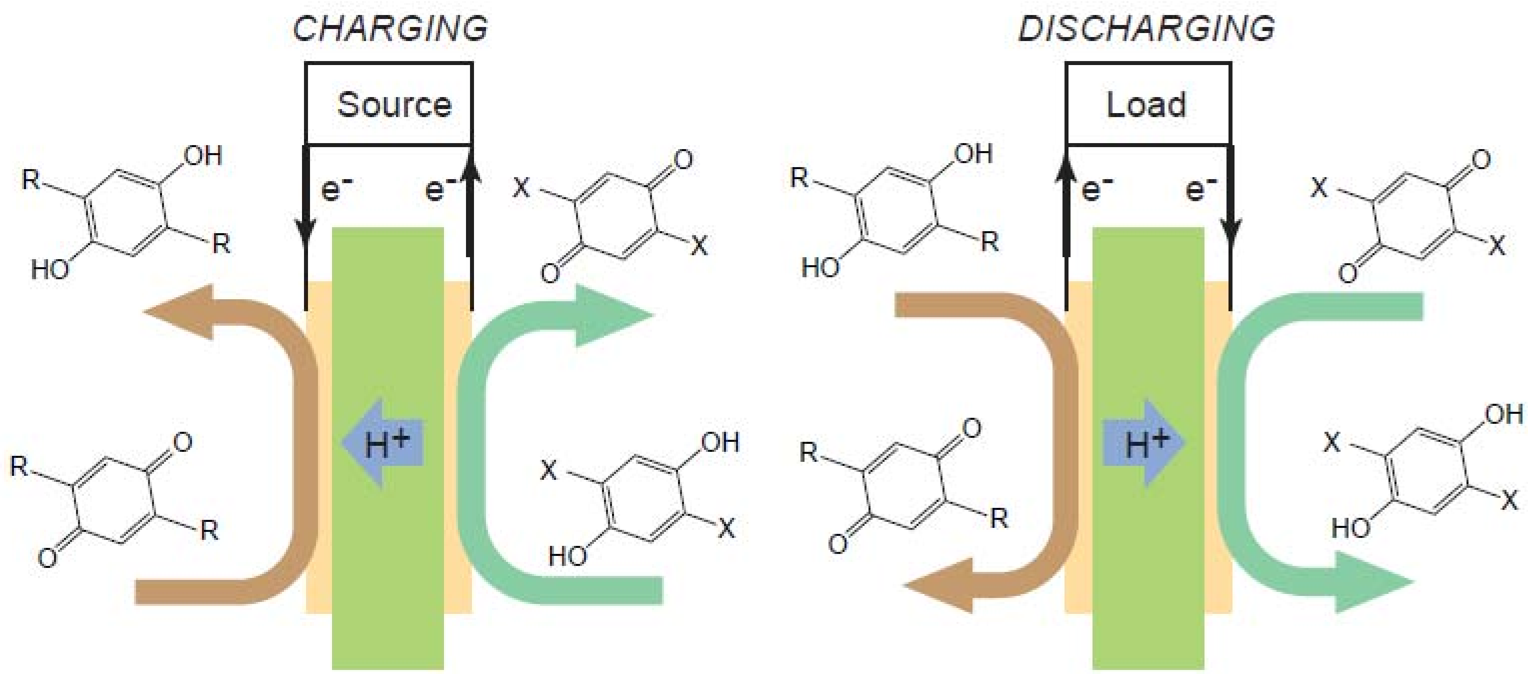
Quinones for Aqueous Flow Batteries

Plastoquinone in photosynthesis | simplest quinone | change the voltage | raise the aqueous solubility



Hydroquinone

The Vision: Organic-Based Aqueous Flow Batteries

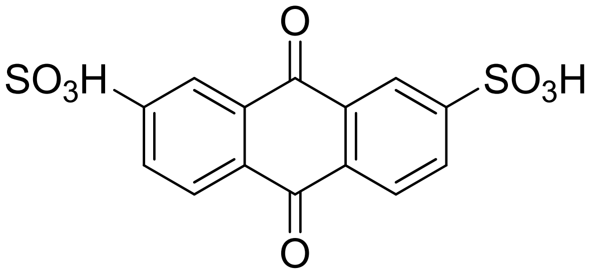


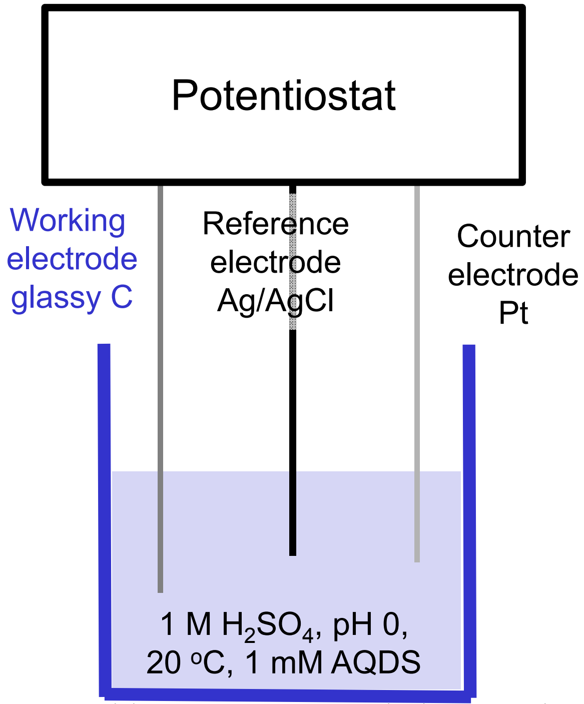
Primary requirements:

- Reduction potential
- Aqueous Solubility
- Redox kinetics
- Stability
- Cost

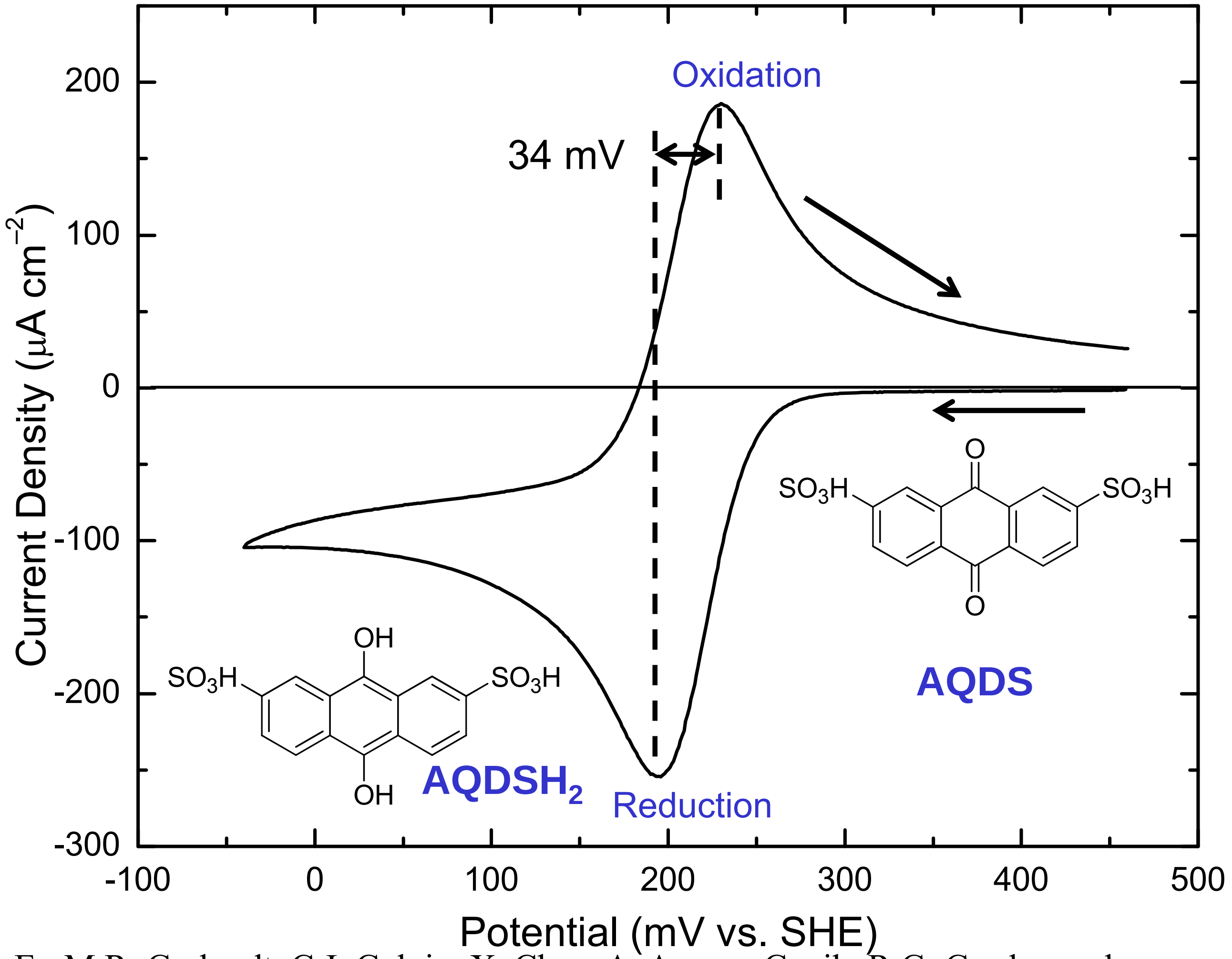
Anthraquinone Di-sulfonate (AQDS)

AQDS





$$AQDSH_2 \underset{Red}{\overset{Ox}{\rightleftharpoons}} AQDS + 2H^+ + 2e^-$$

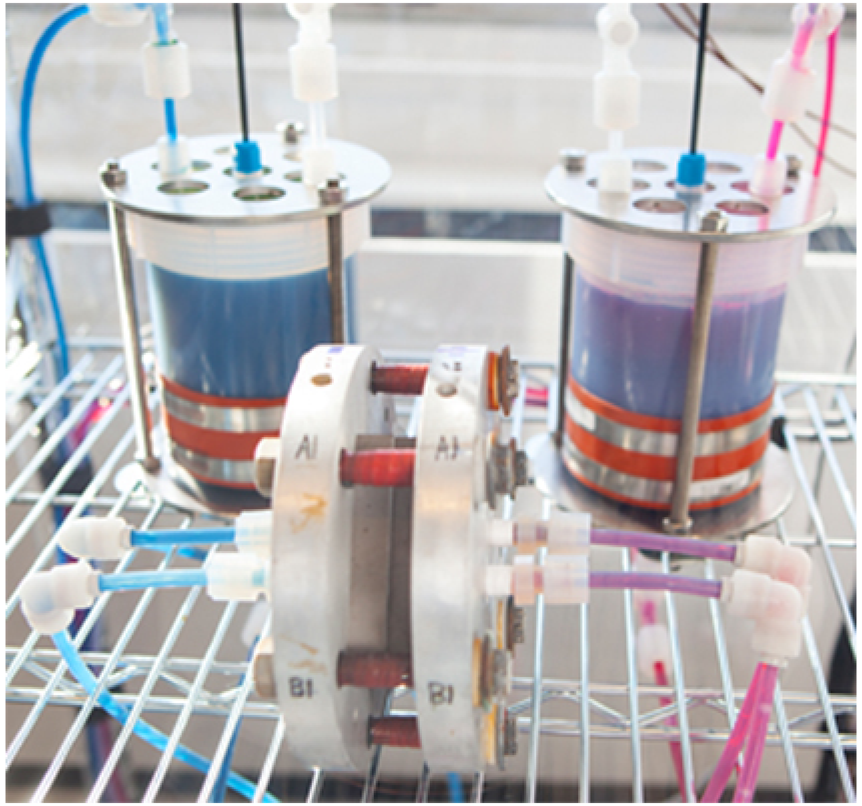


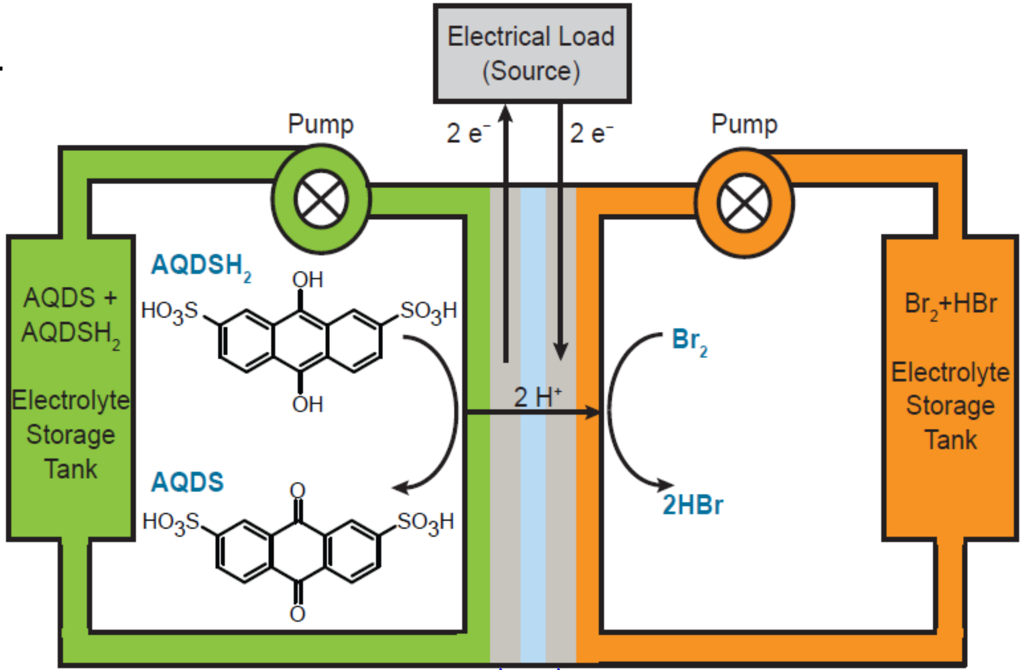
B. Huskinson, M.P. Marshak, C. Suh, S. Er, M.R. Gerhardt, C.J. Galvin, X. Chen, A. Aspuru-Guzik, R.G. Gordon and M.J. Aziz, "A metal-free organic-inorganic aqueous flow battery", *Nature* **505**, 195 (2014)

Quinone-Bromide Flow Battery

$$\mathrm{AQDSH_2} \underset{\text{Red}}{\overset{\text{Ox}}{\rightleftharpoons}} \mathrm{AQDS} + 2H^+ + 2e^-$$

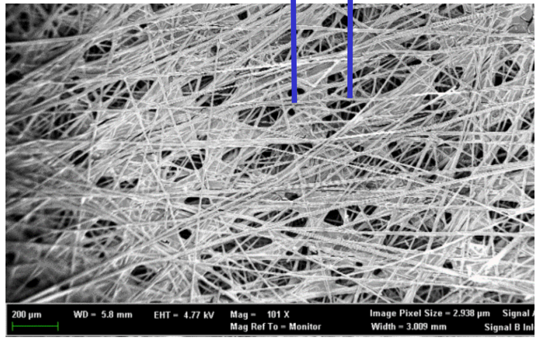
Solubility: 2.8 (moles electrons)/L = 75 Ah/L





$E^0 = +0.21$ V

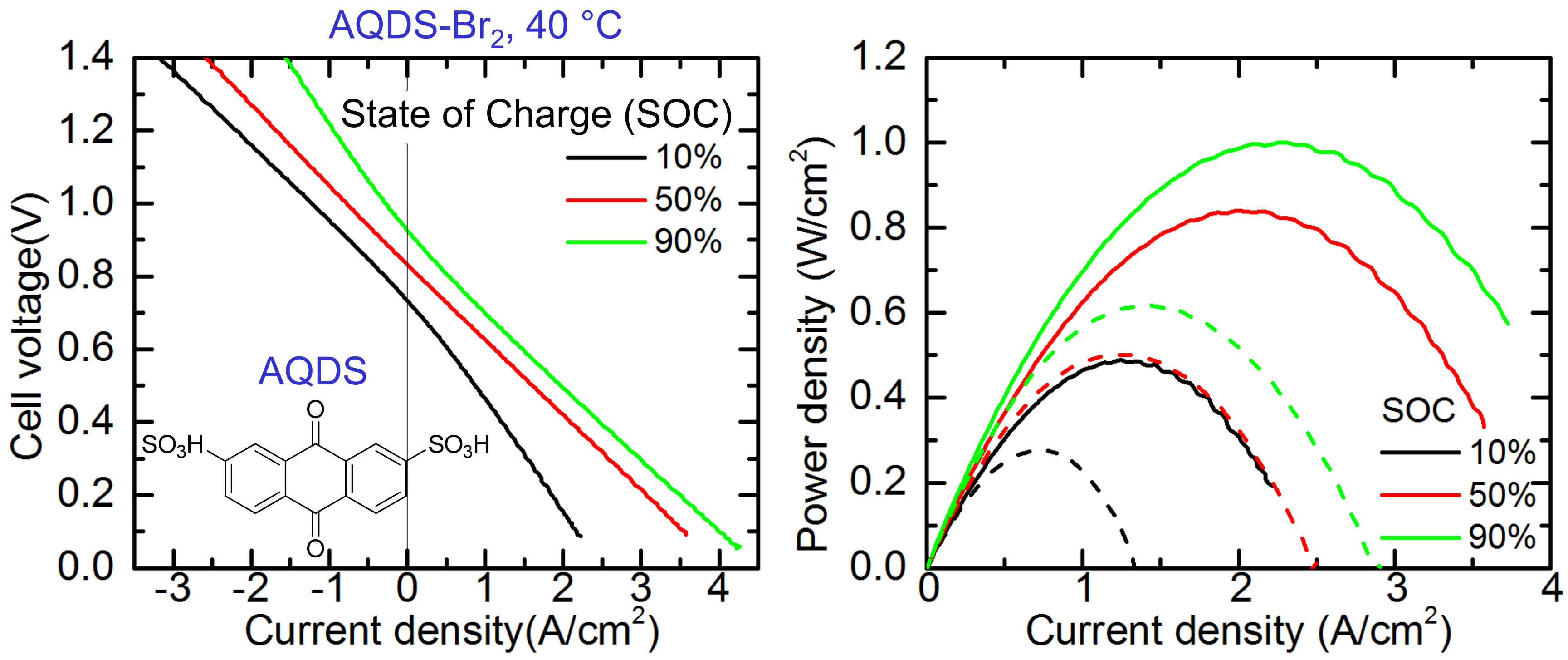
$E^0 = +1.09$ V



Porous carbon paper electrode **(no catalyst)**

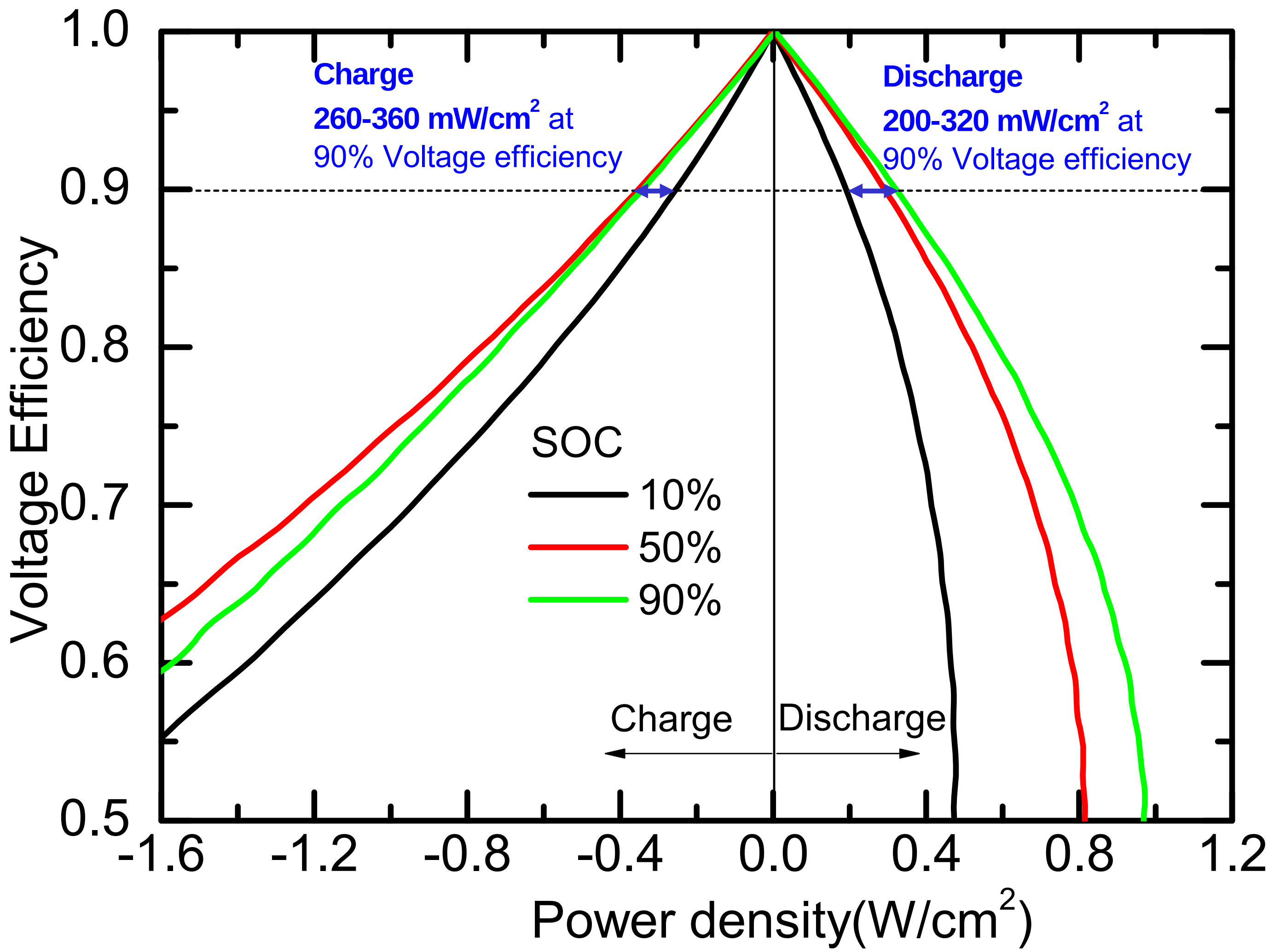
B. Huskinson, M.P. Marshak, C. Suh, S. Er, M.R. Gerhardt, C.J. Galvin, X. Chen, A. Aspuru-Guzik, R.G. Gordon and M.J. Aziz, "A metal-free organic-inorganic aqueous flow battery", *Nature* **505**, 195 (2014)

AQDS-Bromide Cell Performance



Q. Chen, M.R. Gerhardt, L. Hartle, and M.J. Aziz, "A quinone-bromide battery with 1 W/cm^2 power density",
J. Electrochem. Soc. **163**, A5010 (2016), doi: 10.1149/2.0021601jes

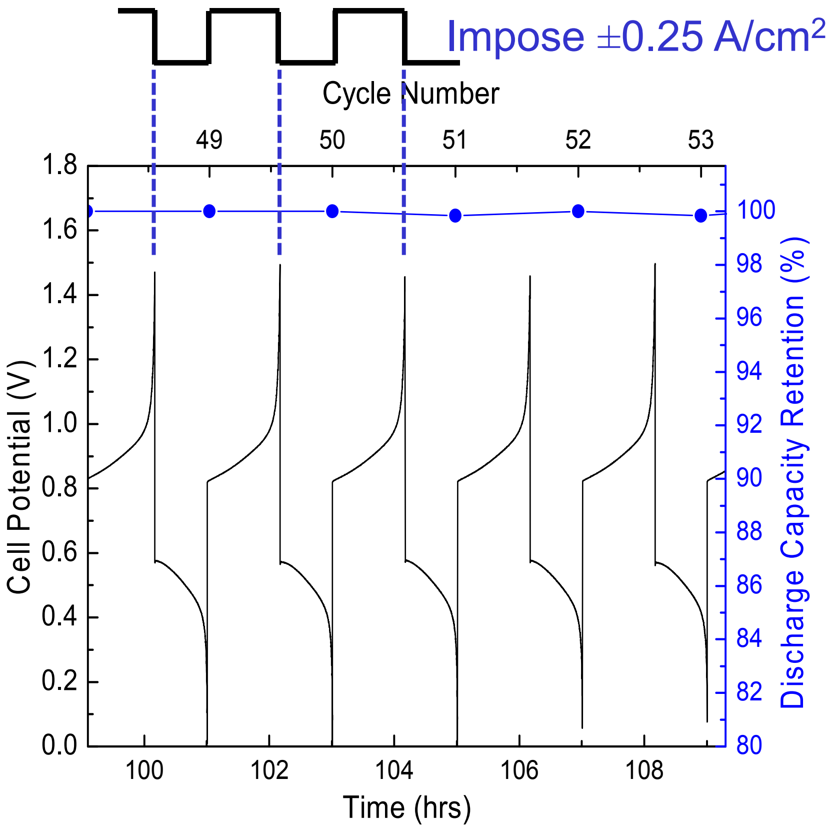
Voltage Efficiency



Deep Cycling Behavior

Capacity Retention Rate = (Coulombs of discharge) / (immediately preceding Coulombs of discharge)

Impose ±0.25 A/cm^2 square wave, switched at 0, +1.5 V



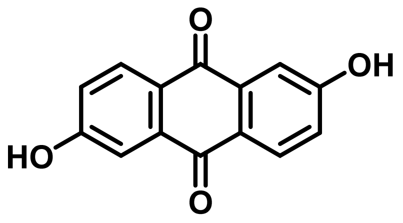
B. Huskinson, M.P. Marshak, M.R. Gerhardt and M.J. Aziz,
"Cycling of a quinone-bromide flow battery for large-scale electrochemical energy storage", *ECS Trans.* **61**, 27 (2014)

Halogen-Free Alkaline Flow Cell

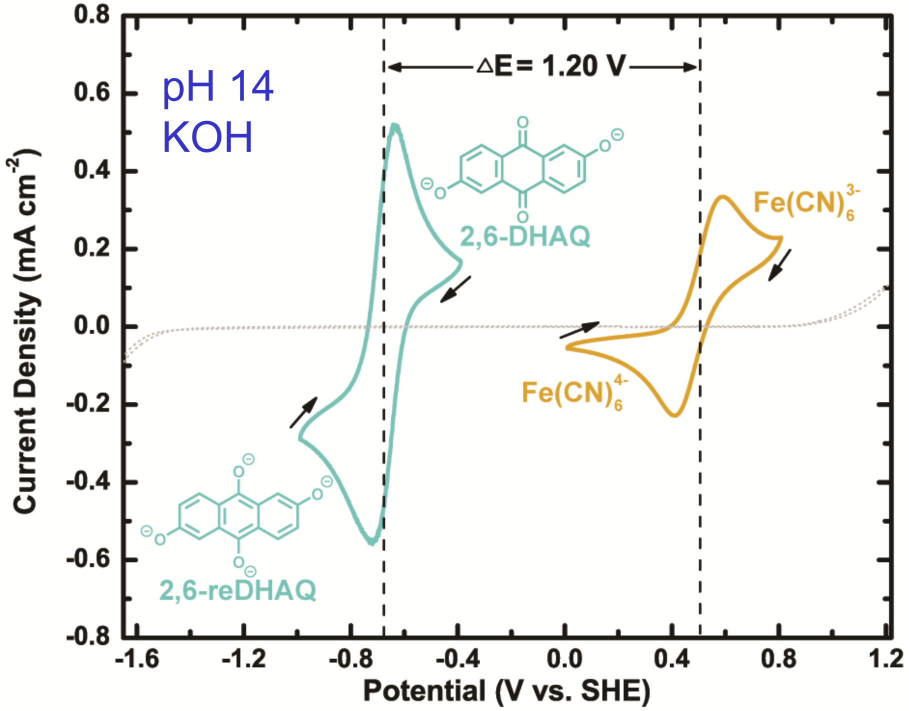
DHAQ-$Fe(CN)_6$

Negolyte: DHAQ in KOH
  Solubility: 1.2 (moles electrons)/L
  = 32 Ah/L
  pH range ~10-14+

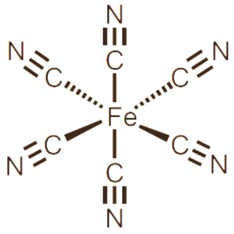
Alkaline quinone negolyte 2,6-DHAQ
Against bromine-free "food additive"† posolyte $Fe(CN)_6$‡



2,6-dihydroxyanthraquinone



Posolyte: $Fe(CN)_6$ in KOH
  pH range ~9-14+
  Solubility: 0.4 (moles electrons)/L
  = 11 Ah/L



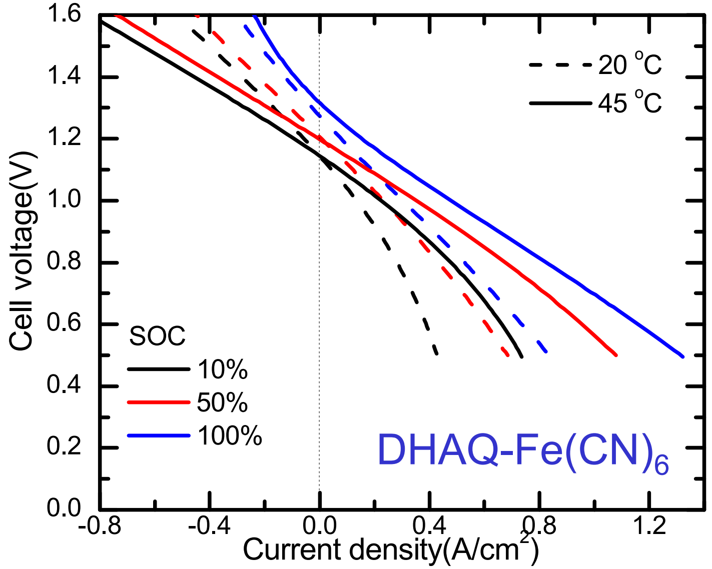
Membrane
  Nafion 212, passing K+

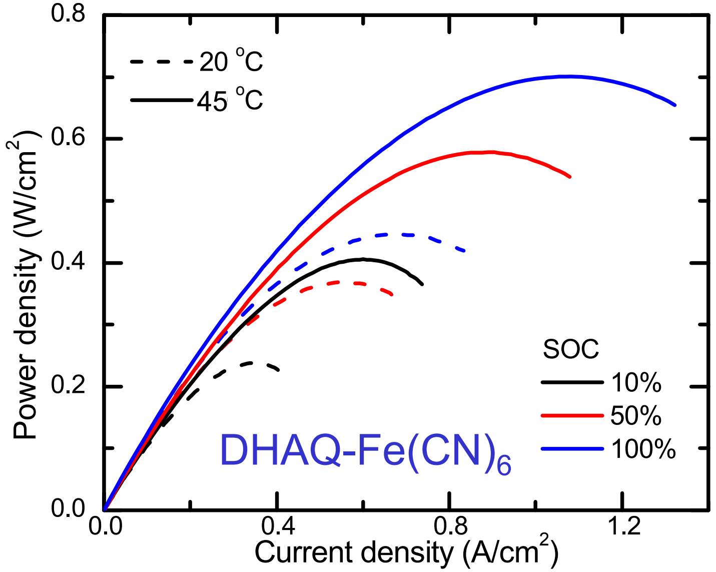
Kaixiang Lin, Q. Chen, M. Gerhardt, L. Tong, S.B. Kim, L. Eisenach, A. Valle, D. Hardee, R.G. Gordon, M.J. Aziz & M.P. Marshak, "Alkaline Quinone Flow Battery", *Science* **349**, 1529 (2015).

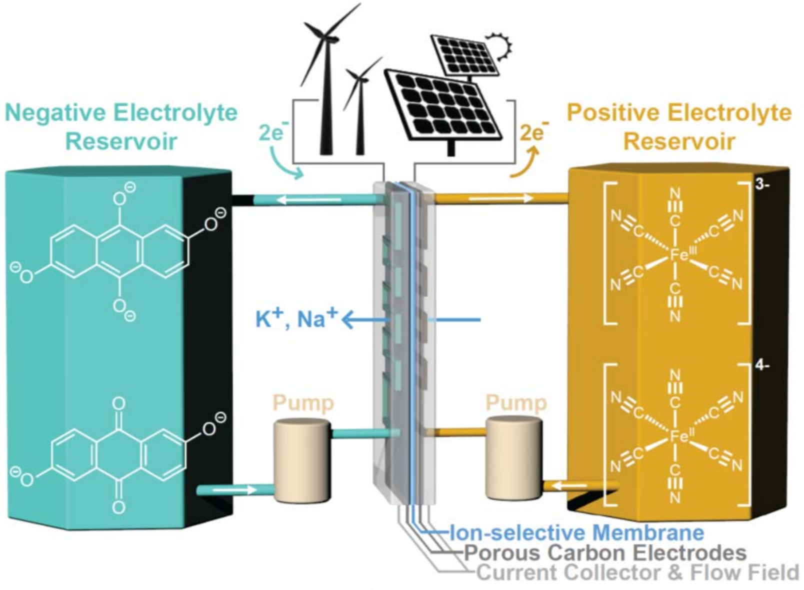
†Seventeenth Report of the Joint FAO/WHO Expert Committee on Food Additives. Report No. 539, *Wld Hlth Org. techn. Rep. Ser.* (539, World Health Organization, 1974).

‡R.P. Hollandsworth, J . Zegarski and J .R. Selman, Zinc/ferricyanide battery development. Phase IV, SAND85-7195, Sandia National Laboratories, May 1985.

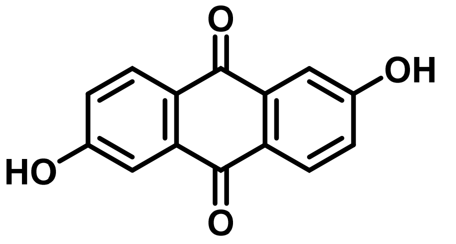
Alkaline Quinone Flow Battery





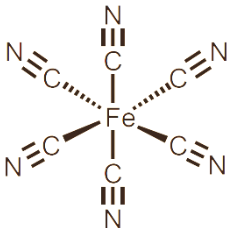


DHAQ



2,6-dihydroxyanthraquinone

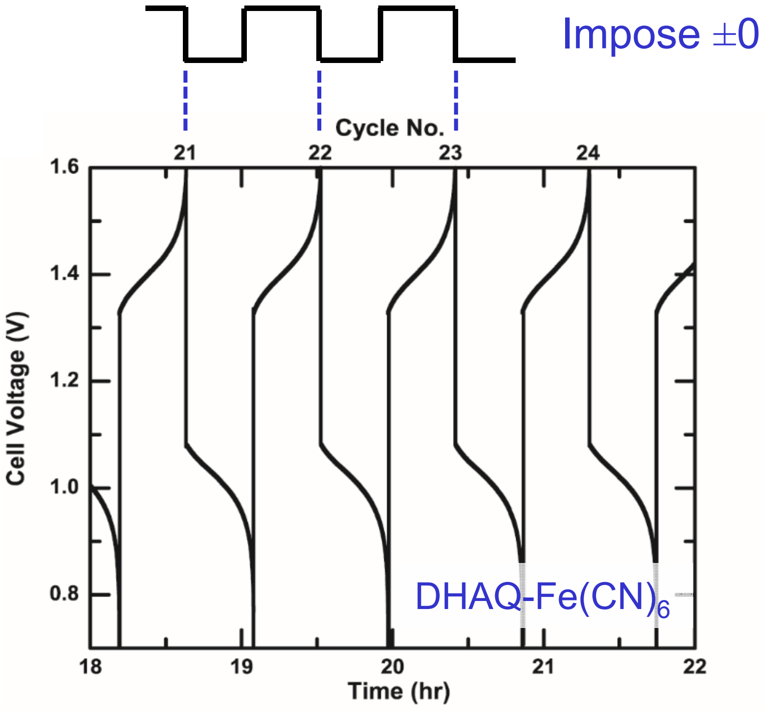
$Fe(CN)_6$



K. Lin, Q. Chen, M. Gerhardt, L. Tong, S.B. Kim, L. Eisenach, A. Valle, D. Hardee, R.G. Gordon, M.J. Aziz & M.P. Marshak, "Alkaline Quinone Flow Battery", *Science* **349**, 1529 (2015).

Robust Quinones

Impose ±0.1 A/cm^2 square wave, switched at 0.7, 1.6 V



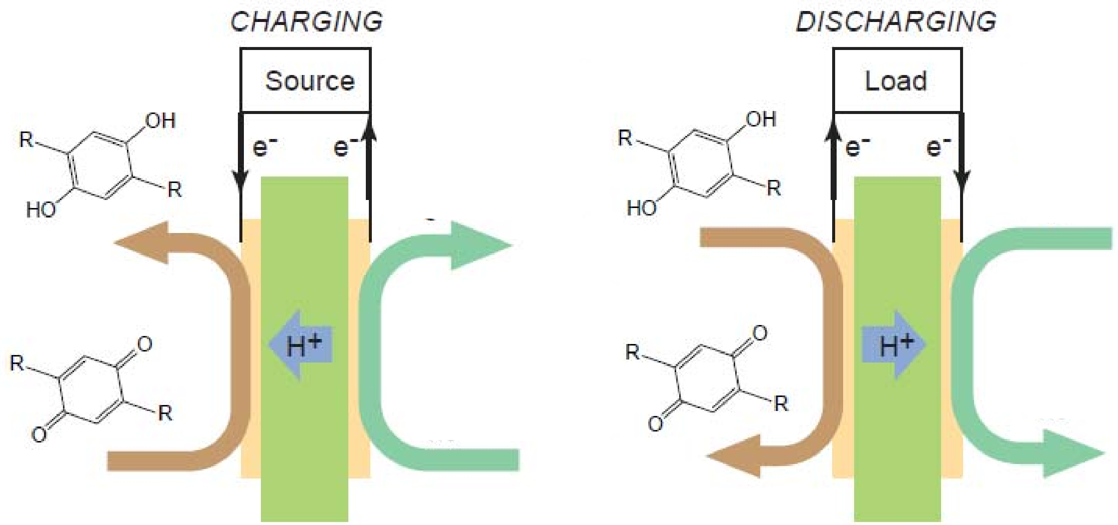
- 99.1% current efficiency
- 99.9% capacity retention per cycle over 100 cycles (latest →99.994%)

Current Efficiency = (Coulombs of discharge) / (coulombs of charge)
Cumulative Capacity Retention = (Coulombs of discharge) / (original Coulombs of discharge)

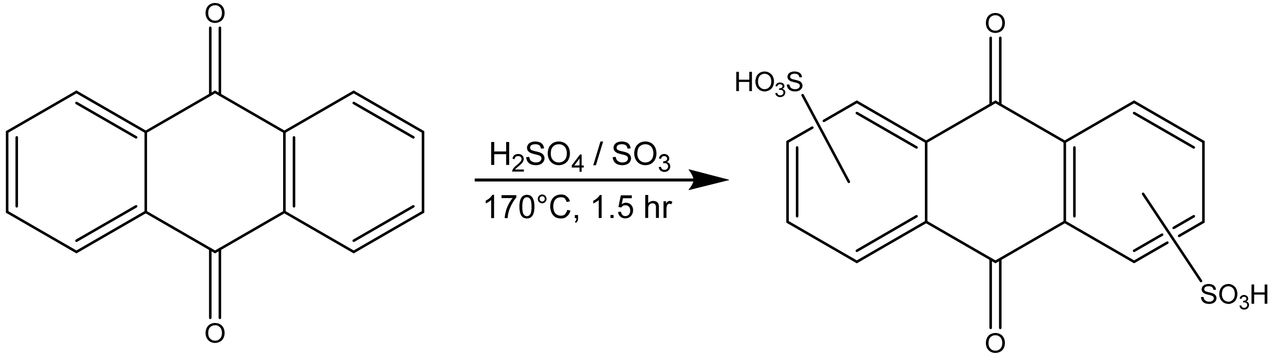
Kaixiang Lin, Q. Chen, M. Gerhardt, L. Tong, S.B. Kim, L. Eisenach, A. Valle, D. Hardee, R.G. Gordon, M.J. Aziz & M.P. Marshak, "Alkaline Quinone Flow Battery", *Science* **349**, 1529 (2015).

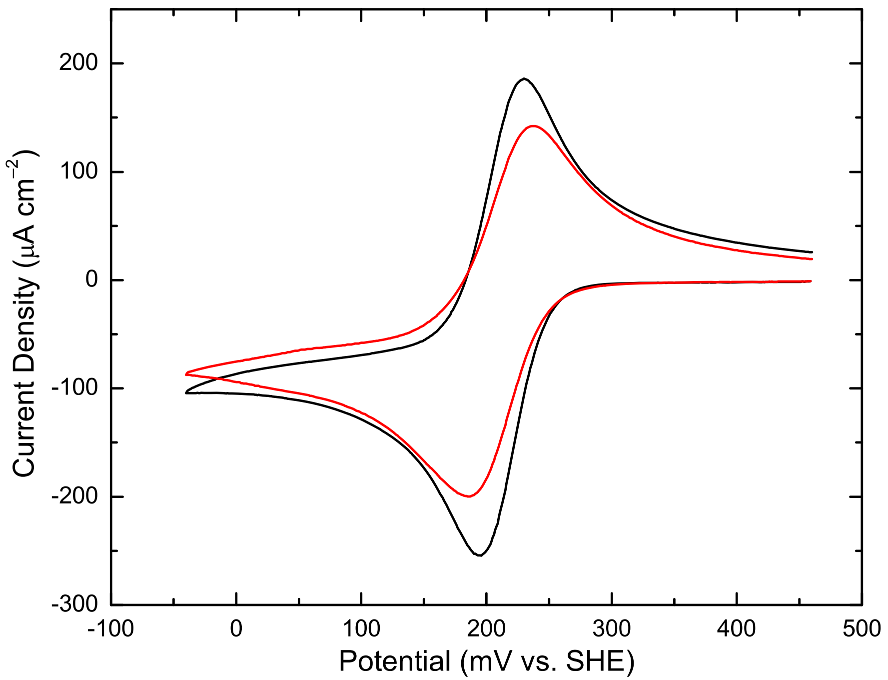
Quinones for Energy Storage

Low chemicals cost:	Enables low cost/kWh
Rapid redox kinetics:	Enable low area/kW → low cost/kW
All-liquid storage:	Enables inexpensive BOS and high cycle life
Aqueous electrolyte:	Enables fireproof operation
Non-toxic:	Ideal for commercial, residential markets
Scalability:	Enables rapid chemistry scaleup
Tunability:	Enables performance improvements
Small organic molecules:	Enable inexpensive separator → low cost/kW



Scalability





Bulk synthesis of AQDS mixtures without purification leads to nearly identical cell performance.

Quinones for Energy Storage

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All-liquid storage:	Enables inexpensive BOS and high cycle life
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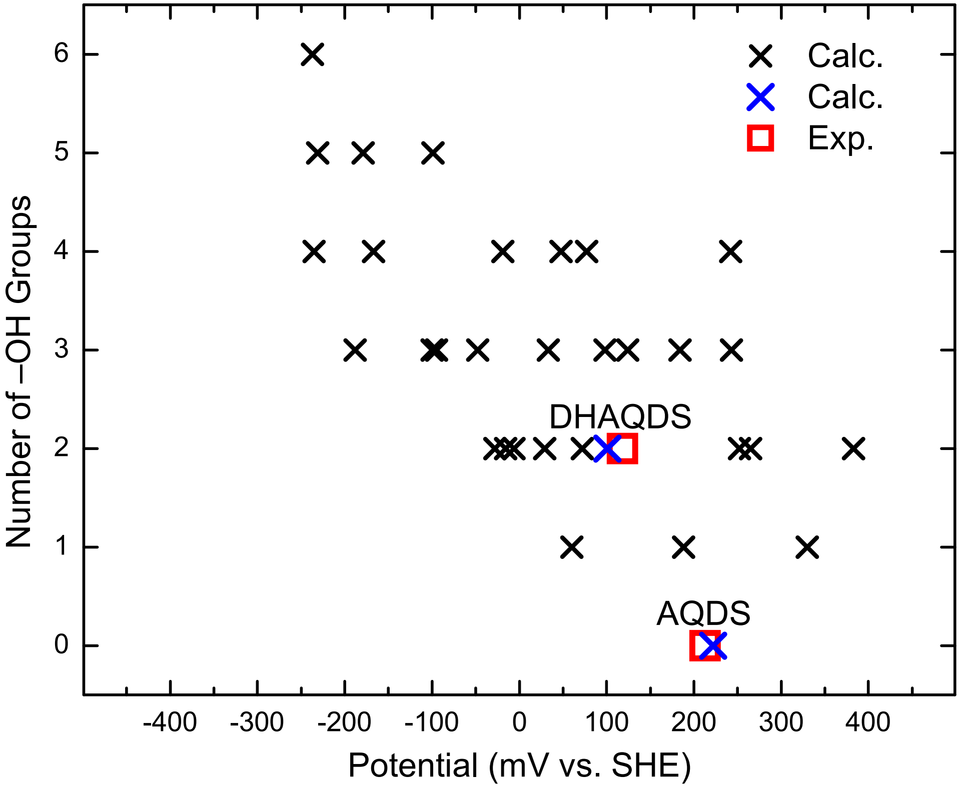
Non-toxic:	Ideal for commercial, residential markets
Scalability:	Enables rapid chemistry scaleup
Tunability:	Enables performance improvements

Computational Screening

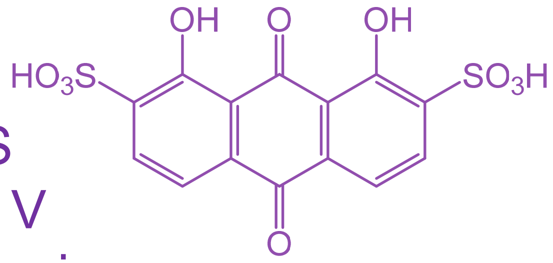
Electron-donating –OH groups lower the reduction potential.



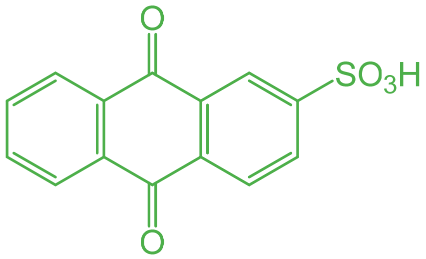
Changwon Suh, Süleyman Er, Michael Marshak, Alán Aspuru-Guzik, "Computational design of molecules for an all-quinone redox flow battery", *Chem. Sci.* **6**, 885 (2015)

Tunability Demonstration in Quinone-Bromide Cell

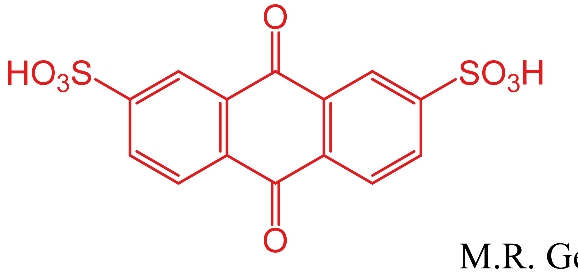
DHAQDS
E^0 = 0.118 V
92 mV OCV gain

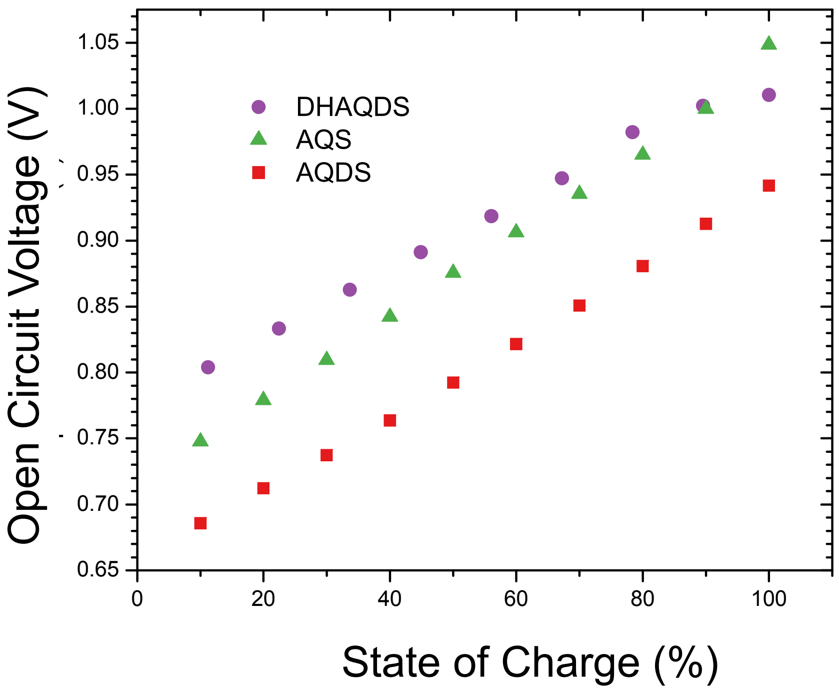


AQS
E^0 = 0.193 V
17 mV OCV gain



AQDS
E^0 = 0.210 V





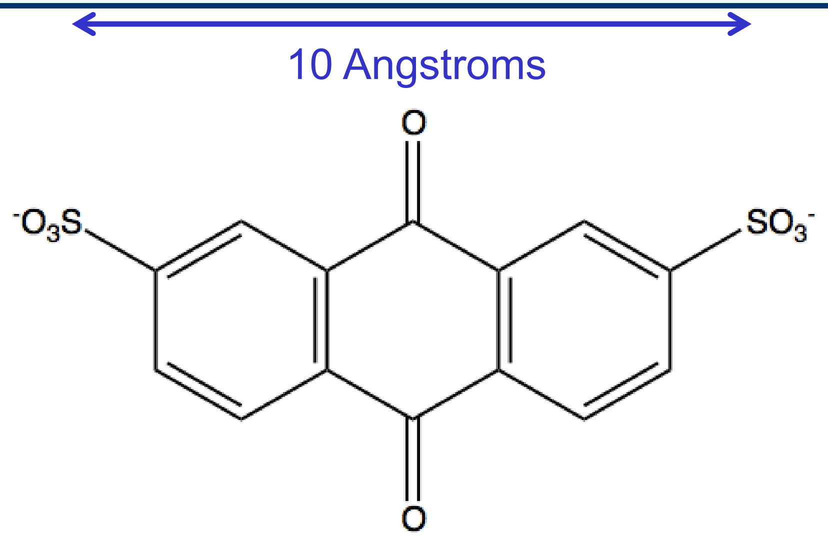
DHAQDS and AQS flow cells against HBr/Br_2 show open circuit voltage rising above 1.0 V at high state of charge.

M.R. Gerhardt, L. Tong, R. Gómez-Bombarelli, Q. Chen, M.P. Marshak, C.J. Galvin, A. Aspuru-Guzik, R.G. Gordon, M.J. Aziz, "Anthraquinone derivatives in aqueous flow batteries", *Adv. Energy Materials* 2016, 1601488.

Posolyte: 0.5 M Br_2, 3 M HBr
Negolyte: 1 M quinone in H_2SO_4 (3 M H^+)

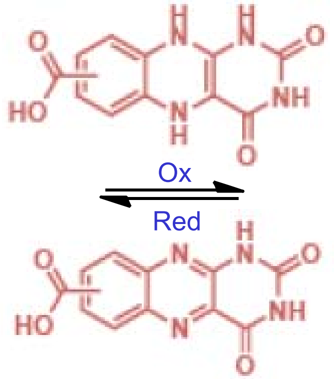
Quinones for Energy Storage

Low chemicals cost:	Enables low cost/kWh
Rapid redox kinetics:	Enable low area/kW → low cost/kW
All-liquid storage:	Enables inexpensive BOS and high cycle life
Aqueous electrolyte:	Enables fireproof operation
Non-toxic:	Ideal for commercial, residential markets
Scalability:	Enables rapid chemistry scaleup
Tunability:	Enables performance improvements
Small organic molecules:	Enable inexpensive separator → low cost/kW



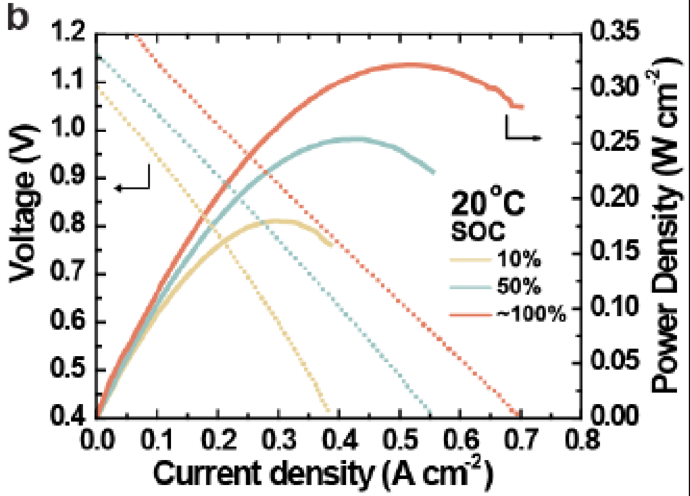
Beyond Quinones: Aza-aromatics for Flow Batteries

Negative couple:
Alloxazine 7/8-carboxylic acid (ACA)
Solubility: 4 mol e^-/L
= 107 Ah/L

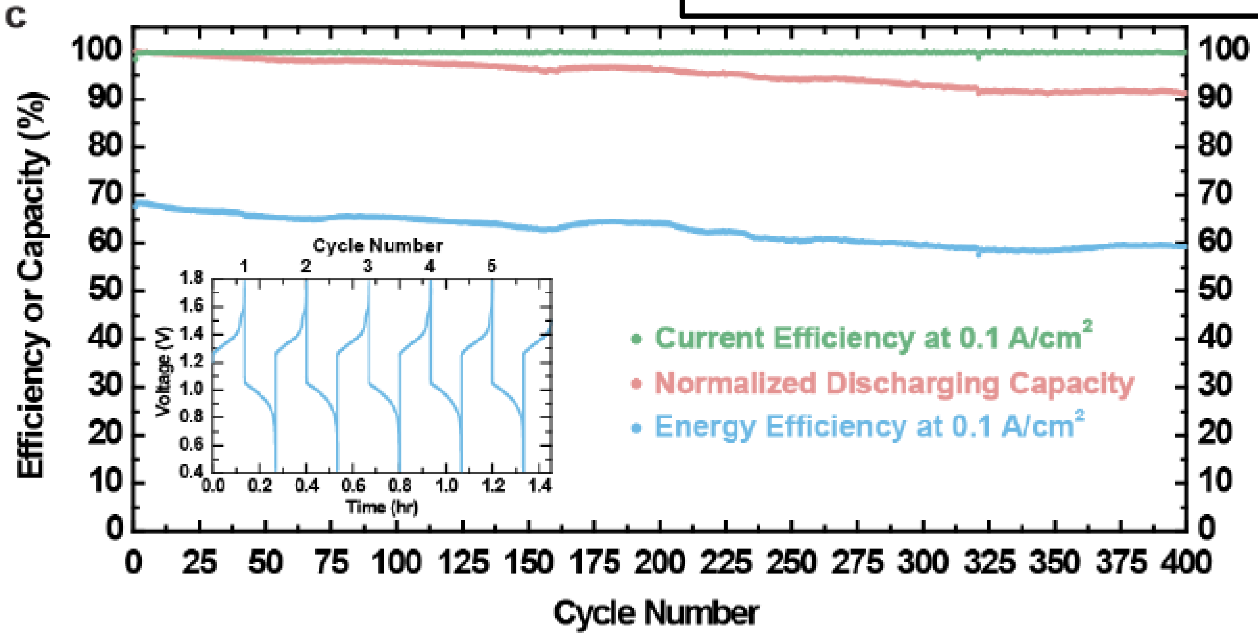


Positive couple:
$Fe(CN)_6$

K. Lin, R. Gómez-Bombarelli, E. Beh, L. Tong, Q. Chen, A. Valle, A. Aspuru-Guzik, R.G. Gordon, M.J. Aziz, "A redox flow battery with an alloxazine-based organic electrolyte", *Nature Energy* **1**, 16102 (2016)



- Average current efficiency over **400 cycles** is **> 99.7%** (negligible side reactions).
- Cell showed **5% capacity loss over 400 cycles** or ~ 0.013% capacity loss per cycle
- Peak power density at R.T. approaches **1/3 W cm^{-2}**

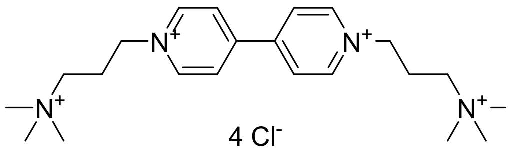


A pH 7 Aqueous Flow Battery with High Capacity

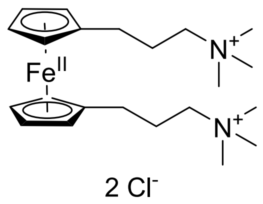
Negolyte: **BTMAP-Viologen**
0.75 M (20.1 Ah/L); 7.5 mL
solubility: 2 M (54 Ah/L)

Posolyte: **BTMAP-Ferrocene**
1.0 M (26.8 Ah/L); 3.25 mL
solubility: 1.9 M (51 Ah/L)
capacity-limiting side

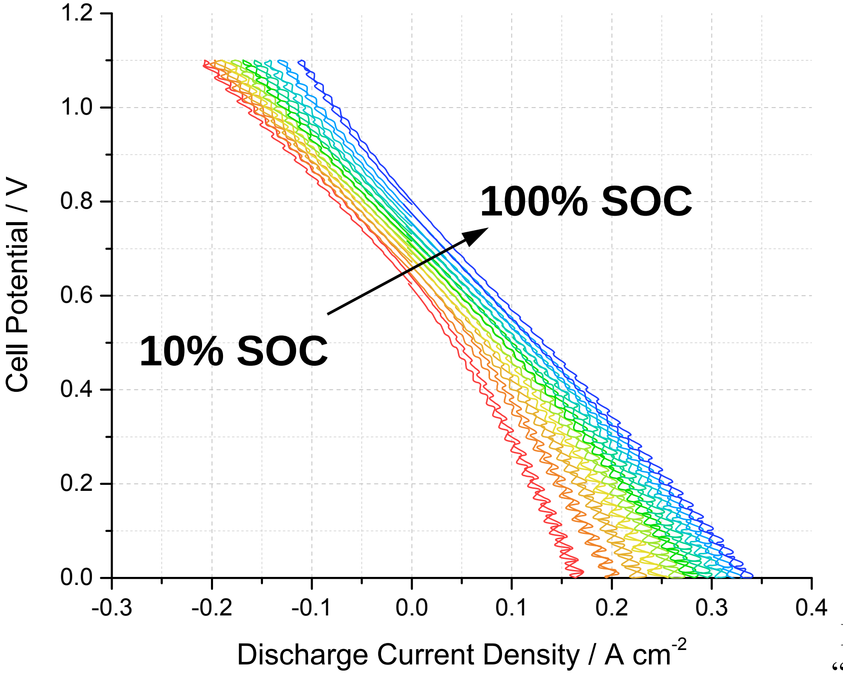
BTMAP-Vi

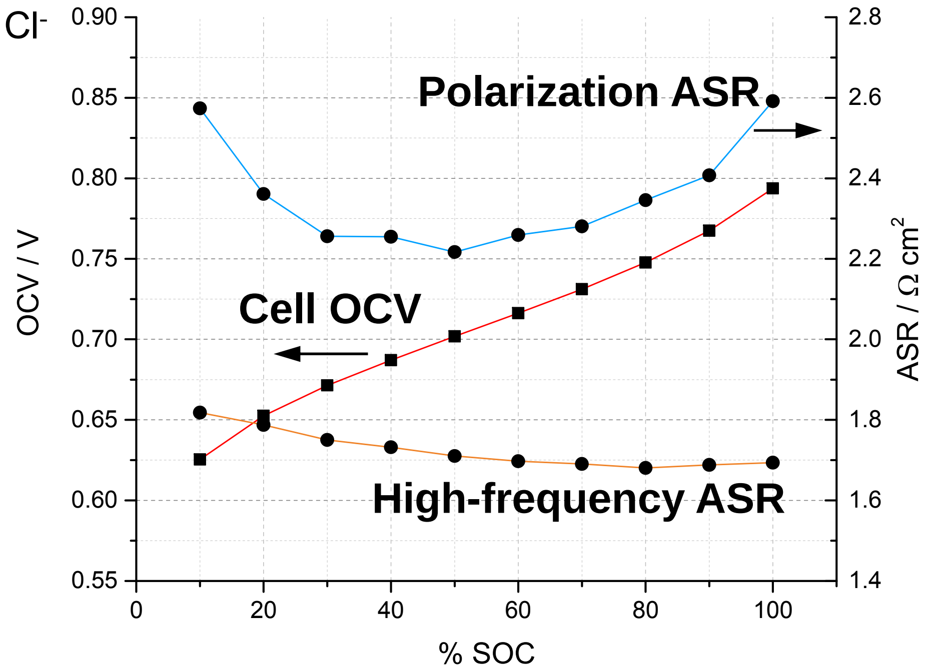


BTMAP-Fc



Membrane: **Selemion DSV**, 110 um, 5 cm^2, conducting Cl^-





Eugene Beh, D. De Porcellinis, R.L. Gracia, K.T. Xia, R.G. Gordon and M.J. Aziz,
"A neutral pH organic/organometallic RFB with extremely high capacity retention"
ACS Energy Lett., in press, pubs.acs.org/doi/abs/10.1021/acsenergylett.7b00019

Record Deep-Cycling Capacity Retention Rate

Negolyte: **BTMAP-Viologen**
0.75 M (20.1 Ah/L); 7.5 mL
solubility: 2 M (54 Ah/L)

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1.0 M (26.8 Ah/L); 3.25 mL
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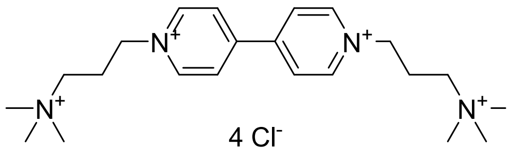
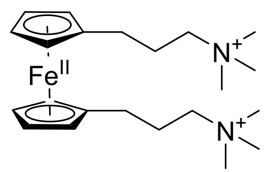
BTMAP-Vi



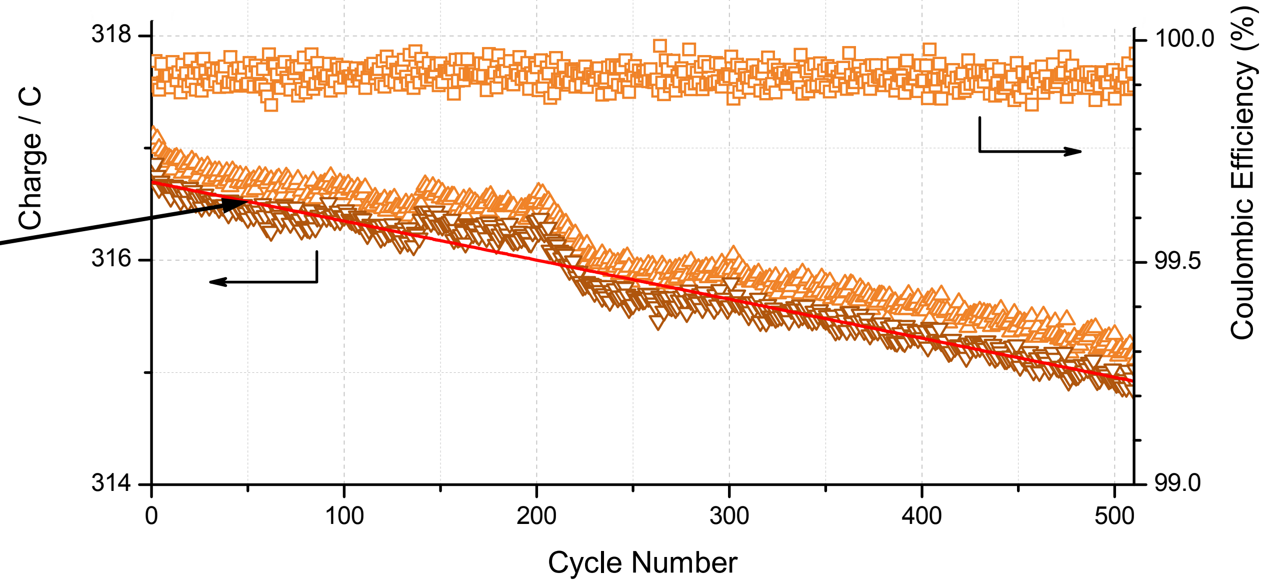
BTMAP-Fc



Membrane: **Selemion DSV**, 110 um, 5 cm^2, conducting Cl$^-$

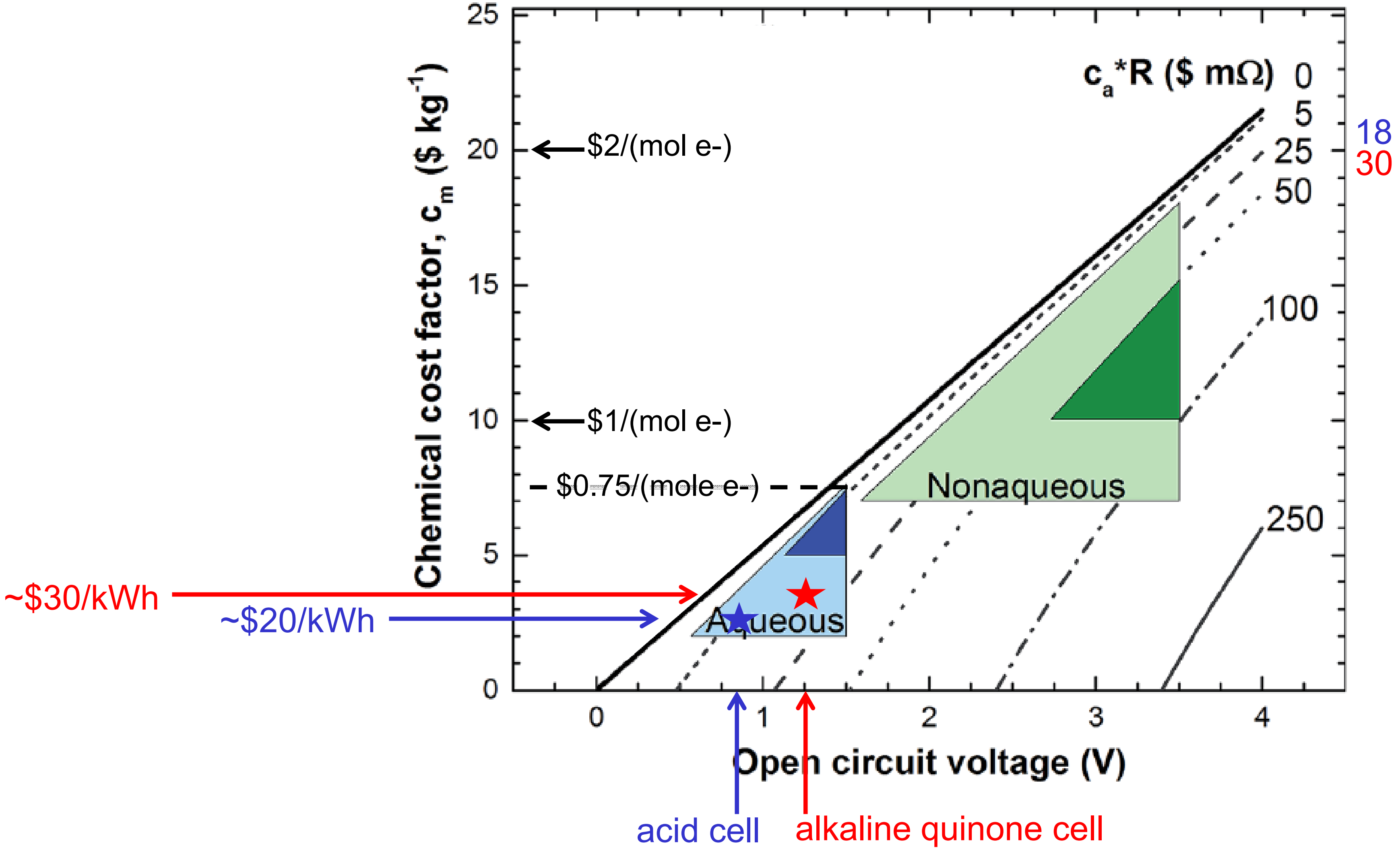
Best fit line for cycles 10-510: Capacity fade rate
0.0011 % /cycle
(→ 1.1% / kilocycle);

0.03%/day
(→ 10.4% / year)



Eugene Beh, D. De Porcellinis, R.L. Gracia, K.T. Xia, R.G. Gordon and M.J. Aziz, "A neutral pH organic/organometallic RFB with extremely high capacity retention" *ACS Energy Lett.*, in press, pubs.acs.org/doi/abs/10.1021/acsenergylett.7b00019

Prospects for $120/kWh (AC-AC)



R.M. Darling, K.G. Gallagher, J.A. Kowalski, S. Ha, and F. Brushett, "Pathways to low-cost electrochemical energy storage: A comparison of aqueous and nonaqueous flow batteries", *Energy & Enviro. Sci.* **7**, 3459 (2014)

Summary and Outlook

Acidic RFB

Quinone - Bromide

- High power density
- Low cost
- Suitable for utility/industrial applications

Alkaline RFB

Quinone - ferrocyanide

- High voltage
- Low toxicity
- High capacity retention rate
- Suitable for residential/ commercial use

Aza-Aromatic RFB

Alloxazine - ferrocyanide

- New class of molecules

Neutral pH RFB

Viologen - ferrocene

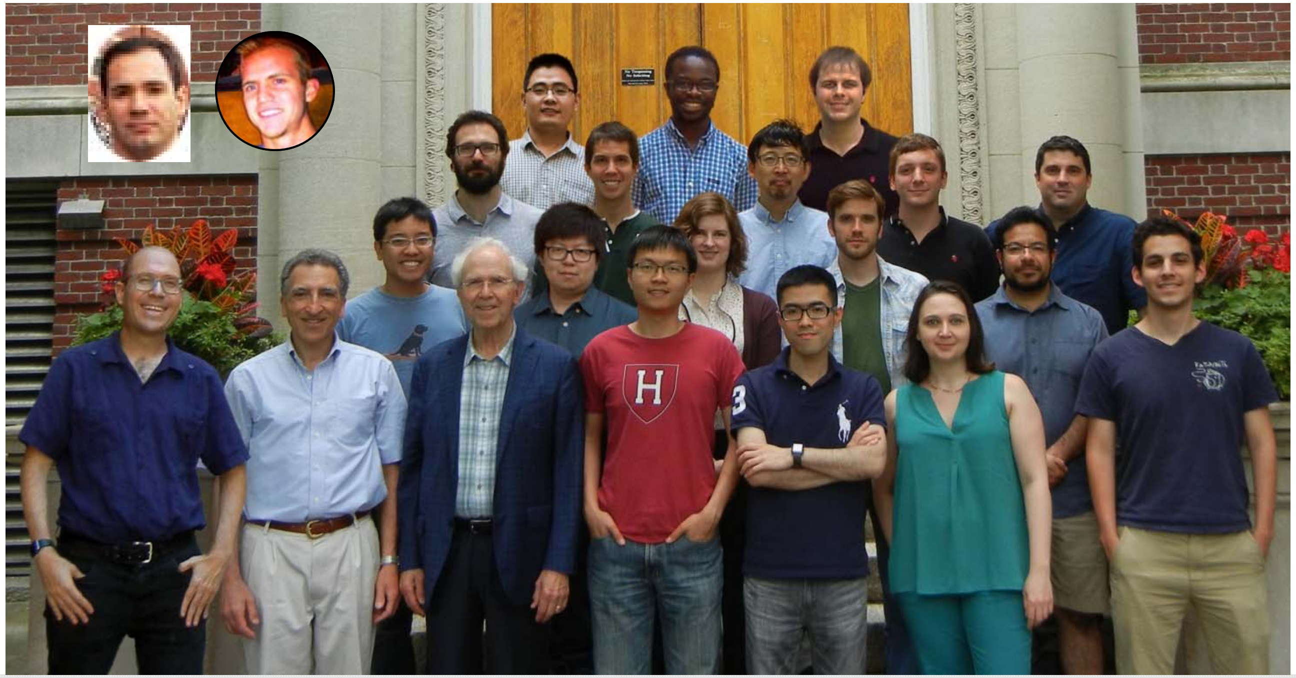
- Low corrosivity
- Record capacity retention rate
- Suitable for residential/

* The cost, tunability, and stability of redox-active organics looks promising for electrical energy storage
* There is a wide range of chemistries to be exploited
* Drop-in replacement?

Harvard Department of Chemistry & Chemical Biology

HARVARD John A. Paulson School of Engineering and Applied Sciences

Acknowledgments



Back to front, left to right:

- Michael Marshak, Brian Huskinson, Zhengjin Yang, David Kwabi, Danny Tabor
- Rafa Gómez-Bombarelli, Andrew Wong, Sungjin “James” Kim, Michael Gerhardt, Joel Veak
- Eugene Beh, Kaixiang Lin, Lauren Hartle, Marc-Antoni Goulet, Prof. Sergio Granados-Focil
- Prof. Alán Aspuru-Guzik, Prof. Michael Aziz, Prof. Roy Gordon, Liuchuan Tong, Qing Chen, Diana De Porcellinis, Alvaro Valle

Not pictured: Professor Ted Betley, Saraf Nawar, Rachel Burton, Cooper Galvin, Rebecca Gracia, Sidharth Chand, Tyler Van Valkenburg, Bilen Aküzüm, Ryan Duncan, Dr. Süleyman Er, Dr. Xudong Chen, Phil Baker, Dr. Trent Molter, Dr. Junling Huang, Prof. Maurizio Salles, Dhruv Pillai, Dr. Changwon Suh, Louise Eisenach, Jennifer Wei

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